The Boltzmann Equation of Phonon Thermal Transport Solved In the Relaxation Time Approximation – I – Theory

The Boltzmann Equation Of Phonon Thermal Transport Solved In the Relaxation Time Approximation – I – Theory

Amelia Carolina Sparavigna[1]

1 – Department of Applied Science and Technology, Politecnico di Torino, Italy


DOI **10.13140/RG.2.1.1001.1923**

Keywords: Thermal Conductivity, Phonons, Boltzmann Equation.

ABSTRACT. The thermal transport of a dielectric solid can be determined by means of the Boltzmann equation regarding its distribution of phonons subjected to a thermal gradient. After solving the equation, the thermal conductivity is obtained. A largely used approach for the solution is that of considering a relaxation time approximation, where the collisions of phonons are represented by relaxation times. This approximation can be questionable, but its use is able of providing reliable information on thermal conductivity and on the role of impurities and lattice defects in the thermal transport. Here we start a discussion on the thermal conductivity in dielectric solids. The discussion is divided in two parts. In the first part, which is proposed in this paper, we analyse the Boltzmann equation and its solution in the relaxation time approximation. In a second part, which will be the subject of a next paper, we will show comparison of calculated and measured thermal conductivities.

Introduction. The thermal transport of dielectric solids can be determined, in a semiclassical approach, by means of the Boltzmann equation, a well-known equation of statistical mechanics used to describe a system not in thermodynamic equilibrium [1-3]. In the case of a dielectric solid, the system is an assembly of phonons, quasiparticles originated from quantization of lattice vibrations, subjected to a thermal gradient. The Boltzmann equation contains a non-equilibrium distribution $g(\mathbf{r},\mathbf{k},t)$, in which arguments $(\mathbf{r},\mathbf{k},t)$ are position, wave-vector and time for the considered particles. The problem of transport is solved when distribution $g(\mathbf{r},\mathbf{k},t)$ is determined and, from it, the thermal conductivity evaluated.

Solving the Boltzmann equation to have the phonon non-equilibrium distribution is a non-trivial task. In particular, it requires the evaluation of phonon scattering mechanisms, which are rendering the equation an integro-differential equation [4-14]. A simple approach to the solution is that of using the relaxation time approximation. This approximation can be questionable because it is not considering the real microscopic properties of the lattice [6,7]; however, its use is able of providing good information on thermal conductivity and on the role impurities and defects in thermal transport. For this reason, the use of relaxation time approximation for solving the Boltzmann equation is an approach, which is still largely used.

The core of a relaxation time approximation is the following. Let us have a particle or a quasi-particle, a phonon for instance, that in the time interval *dt*, is subjected to a collision with probability $\mathrm{d}t/\tau$. We can assume that the time parameter τ is depending on the phonon properties: $\tau=\tau(\mathbf{r},\mathbf{k})$. We assume the variation of the distribution be given by:

$$\mathrm{d}g(\mathbf{r},\mathbf{k},t)=g(\mathbf{r},\mathbf{k},t+\mathrm{d}t)-g(\mathbf{r},\mathbf{k},t)=\frac{\mathrm{d}t}{\tau(\mathbf{r},\mathbf{k})}\,g^{o}(\mathbf{r},\mathbf{k}) \qquad (1)$$

In Eq.1, $g^{o}(\mathbf{r},\mathbf{k})$ is the equilibrium Bose-Einstein distribution. Approximation (1) tells that we assume, for solving the Boltzmann equation, that the distribution of phonons emerging from collisions does not depend on the non-equilibrium distribution $g(\mathbf{r},\mathbf{k},t)$, which we have before the collision. This assumption is reasonable if we are not too far from equilibrium.

As told previously, the relaxation time approximation is still largely used and therefore its discussion can be relevant for researchers who are investigating the thermal transport of solids. Here, we propose a first paper where we discuss how the thermal conductivity of a dielectric solid is determined from the Boltzmann equation. In a next paper, we will continue our analysis, comparing the thermal conductivity evaluated using the relaxation time approximation to experimental data.

Boltzmann equation and thermal conductivity. Phonons, such as electrons, move changing their position and momentum because subjected to diffusion, external fields and collisions. They obey to a general equation, which is the Boltzmann equation.

Let us consider a distribution of particles $g(\mathbf{r},\mathbf{k},t)$. Its general equation is [1]:

$$\frac{\partial g}{\partial t}+\frac{\mathrm{d}\mathbf{r}}{\mathrm{d}t}\cdot\frac{\partial g}{\partial \mathbf{r}}+\frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t}\cdot\frac{\partial g}{\partial \mathbf{k}}=\left(\frac{\partial g}{\partial t}\right)_{\text{collis}} \tag{2}$$

The second term on the left is coming from the migration of particles and the third term is produced by the drift of particles due to an external action, for instance a generalized force $\mathbf{F}$. Equation (2) becomes the Boltzmann equation:

$$\frac{\partial g}{\partial t}+\mathbf{v}\cdot\frac{\partial \mathrm{g}}{\partial \mathbf{r}}+\mathbf{F}\cdot\frac{1}{\hbar}\frac{\partial g}{\partial \mathbf{k}}=\left(\frac{\partial g}{\partial t}\right)_{\text{collis}} \tag{3}$$

When the collision terms are written explicitly, the Boltzmann equation turns out in an integro-differential form. As previously told, this equation is often solved in the relaxation time approximation for an easy comparison to experimental data. Before discussing in detail this approximation, let us describe the Boltzmann equation for phonons.

Phonons are quasiparticles introduced in the harmonic approximation of lattice vibrations by the quantization of vibrational modes. Let us remember that quasiparticles occur when a microscopic system, such as a solid, is modelled by an assembly of different weakly interacting particles in a free space corresponding to the volume occupied by the system. Therefore, the assembly of phonons is a gas where quasiparticles are interacting, producing the thermal transport in the lattice. The cubic terms of the corresponding Hamiltonian function are giving the three-phonons processes, which are distinguished in *normal* and *umklapp* processes. The umklapp processes can transfer momentum to the lattice as a whole, degrading the thermal current.

To solve the Boltzmann equation of phonons, let us suppose a distribution $n_{\mathbf{q}p}(\mathbf{r},t)$, for phonon state (**q**, *p*) about position **r** and time *t*, where **q** is the wave-number and *p* the polarization. Let us suppose a gradient ∇T of temperature $T = T(\mathbf{r})$ giving origin to a diffusion process. In this manner, we have a scalar term of the form:

$$-\mathbf{v}_p(\mathbf{q})\cdot\nabla T\,\frac{\partial n_{\mathbf{q}p}}{\partial T}$$

In it, $\mathbf{v}_p(\mathbf{q})$ is the group velocity of phonon ($\mathbf{q}$, p). The distribution $n_{\mathbf{q}\,p}$ depends on position through the temperature $T = T(\mathbf{r})$. Moreover, scattering processes are changing the distribution.

If we have a stationary condition, the total variation must be equal to zero:

$$-\mathbf{v}_p(\mathbf{q})\cdot\nabla T\,\frac{\partial n_{\mathbf{q}p}}{\partial T}+\left.\frac{\partial n_{\mathbf{q}p}}{\partial t}\right|_{\text{scatt}}=0 \tag{4}$$

Eq.4 is the general form of Boltzmann equation for phonons subjected to a thermal gradient [1-3]. It becomes an integro-differential equation, when the scattering term representing the collisions of quasiparticles is explicitly given.

In the case of a small thermal gradient, the equation is solved linearizing it, by considering just small deviations from equilibrium. The deviation is given by $n_{\mathbf{q}p} - n^{o}_{\mathbf{q}p}$, where $n^{o}_{\mathbf{q}p}$ is the equilibrium distribution. To illustrate the approach, let us consider the case of elastic scattering of phonons, where the phonon process is given by $(\mathbf{q},p)\rightarrow(\mathbf{q}',p')$, with conservation of energy. The probability of a transition from $(\mathbf{q},p)$ to $(\mathbf{q}',p')$, in the time unit, is [1]:

$$P^{\mathbf{q}'p'}_{\mathbf{q}p}=n_{\mathbf{q}p}(n_{\mathbf{q}'p'}+1)Z^{\mathbf{q}'p'}_{\mathbf{q}p} \tag{5}$$

In (5), $Z^{\mathbf{q}'p'}_{\mathbf{q}p}$ is the intrinsic probability, which does not depend on the occupation of phonon states $(\mathbf{q},p)$ and $(\mathbf{q}',p')$. The transition probability from $(\mathbf{q}',p')$ to $(\mathbf{q},p)$ is [1]:

$$\begin{gathered}P^{\mathbf{q}p}_{\mathbf{q}'p'}=n_{\mathbf{q}'p'}(n_{\mathbf{q}p}+1)Z^{\mathbf{q}p}_{\mathbf{q}'p'}\\ Z^{\mathbf{q}p}_{\mathbf{q}'p'}=Z^{\mathbf{q}'p'}_{\mathbf{q}p}\end{gathered} \tag{6}$$

In this manner, we can write the scattering term as [1]:

$$\left.\frac{\partial n_{\mathbf{q}p}}{\partial t}\right|_{\text{scatt}}=\sum_{\mathbf{q}'p'}\left(P^{\mathbf{q}p}_{\mathbf{q}'p'}-P^{\mathbf{q}'p'}_{\mathbf{q}p}\right)=\sum_{\mathbf{q}'p'}\left[n_{\mathbf{q}'p'}(n_{\mathbf{q}p}+1)-n_{\mathbf{q}p}(n_{\mathbf{q}'p'}+1)\right]Z^{\mathbf{q}'p'}_{\mathbf{q}p} \tag{7}$$

And, linearizing it [1]:

$$\left.\frac{\partial n_{\mathbf{q}p}}{\partial t}\right|_{\text{scatt}}=\sum_{\mathbf{q}'p'}\left[(n_{\mathbf{q}'p'}-n^{o}_{\mathbf{q}'p'})-(n_{\mathbf{q}p}-n^{o}_{\mathbf{q}p})\right]Z^{\mathbf{q}'p'}_{\mathbf{q}p} \tag{8}$$

Let us remember that we have, for the equilibrium distribution, $n^o_{\mathbf{q}p} = n^o_{\mathbf{q}'p'}$, because $n^o_{\mathbf{q}p}$ depends on energy only. For the conservation of energy, in the elastic process, $\hbar\,\omega_{\mathbf{q}p} = \hbar\,\omega_{\mathbf{q}'p'}$.

The linearized Boltzmann equation becomes:

$$-\mathbf{v}_p(\mathbf{q})\cdot\nabla T\,\frac{\partial n^o_{\mathbf{q}p}}{\partial T} = \sum_{\mathbf{q}'p'}\left[(n_{\mathbf{q}p} - n^o_{\mathbf{q}p}) - (n_{\mathbf{q}'p'} - n^o_{\mathbf{q}'p'})\right] Z^{\mathbf{q}'p'}_{\mathbf{q}p} \tag{9}$$

In the equation, $(\partial n_{\mathbf{q}\,p} / \partial T)$ is given only by the contribution of the equilibrium distribution $n^o_{\mathbf{q}p}$. To have the Boltzmann linearized equation in the general case, let us define $\Psi_{\mathbf{q}\,p}$ as:

$$n_{\mathbf{q}p} = n^o_{\mathbf{q}p} - \Psi_{\mathbf{q}p}\,\frac{\partial n^o_{\mathbf{q}p}}{\partial(\hbar\omega_{\mathbf{q}p})} \tag{10}$$

Let us remember that ($x = \hbar\omega_{\mathbf{q}p}\big/k_BT$; k_B is the Boltzmann constant):

$$\frac{1}{\mathrm{k}_B T}\frac{\partial}{\partial x}\left\{\frac{1}{e^x - 1}\right\} = \frac{1}{\mathrm{k}_B T}\,n_{\mathbf{q}p}\left(n_{\mathbf{q}p} + 1\right)$$

Then, in the case of elastic scattering, the linearized equation is [7]:

$$-\mathrm{k_B}\,T\,\mathbf{v}_p(\mathbf{q})\cdot\nabla T\,\frac{\partial n^o_{\mathbf{q}p}}{\partial T} = \sum_{\mathbf{q}'p'}\left[\Psi_{\mathbf{q}p}\,n^o_{\mathbf{q}p}(n^o_{\mathbf{q}p}+1) - \Psi_{\mathbf{q}'p'}\,n^o_{\mathbf{q}'p'}(n^o_{\mathbf{q}'p'}+1)\right] Z^{\mathbf{q}'p'}_{\mathbf{q}p} \tag{11}$$

$$\begin{gathered}\mathrm{k_B}\,T\,\mathbf{v}_p(\mathbf{q})\cdot\nabla T\,\frac{\partial n^o_{\mathbf{q}p}}{\partial T} = \sum_{\mathbf{q}'p'}\left[\Psi_{\mathbf{q}'p'} - \Psi_{\mathbf{q}p}\right] Q^{\mathbf{q}'p'}_{\mathbf{q}p} \\ Q^{\mathbf{q}'p'}_{\mathbf{q}p} = n^o_{\mathbf{q}p}(n^o_{\mathbf{q}p}+1)\,Z^{\mathbf{q}'p'}_{\mathbf{q}p}\end{gathered} \tag{12}$$

In the case of three-phonon scattering, the linearized equation is [7]:

$$\begin{aligned}\mathrm{k_B}\,T\,\mathbf{v}_p(\mathbf{q})\cdot\nabla T\,\frac{\partial n^o_{\mathbf{q}p}}{\partial T} = {} & \sum_{\mathbf{q}'p'}\sum_{\mathbf{q}''p''} Q^{\mathbf{q}''p''}_{\mathbf{q}p,\mathbf{q}'p'}\left[\Psi_{\mathbf{q}''p''} - \Psi_{\mathbf{q}'p'} - \Psi_{\mathbf{q}p}\right] + \\ & + \frac{1}{2}\sum_{\mathbf{q}'p'}\sum_{\mathbf{q}''p''} Q^{\mathbf{q}'p',\mathbf{q}''p''}_{\mathbf{q}p}\left[\Psi_{\mathbf{q}''p''} + \Psi_{\mathbf{q}'p'} - \Psi_{\mathbf{q}p}\right]\end{aligned} \tag{13}$$

Summations on $\mathbf{q}'$ and $\mathbf{q}''$ concern phonons in the Brillouin Zone of the lattice. However, it is better to change the summation into an integration as:

$$\sum_{\mathbf{q}'} \rightarrow \frac{\Omega}{(2\pi)^3} \int \mathrm{d}^3\mathbf{q}'$$

$\Omega = NV$ is the volume of the crystal, N the number of primitive cells of it, having volume V. Once function $\Psi_{\mathbf{q}p}$ is evaluated, with the iterative method [6,7] for instance, the density of the thermal current $\mathbf{U}$ can be determined. This density current is defined as:

$$\mathbf{U} = \frac{1}{\Omega} \sum_{\mathbf{q}p} \hbar\omega_{\mathbf{q}p} \mathbf{v}_{\mathbf{q}p} n_{\mathbf{q}p} = -\frac{1}{\Omega} \sum_{\mathbf{q}p} \hbar\omega_{\mathbf{q}p} \mathbf{v}_{\mathbf{q}p} \frac{\partial n^o_{\mathbf{q}p}}{\partial(\hbar\omega_{\mathbf{q}p})} \Psi_{\mathbf{q}p} \tag{14}$$

In a Cartesian frame having unit vectors $\mathbf{u}_i$, current $\mathbf{U}$ is:

$$U_j = -\sum_i \kappa_{ji} \frac{\partial T}{\partial x_i} \tag{15}$$

Tensor κ_{ij} is the thermal conductivity tensor, that, in a isotropic crystal is having non-null terms $\kappa_{xx} = \kappa_{yy} = \kappa_{zz} = \kappa$.

Phonon collisions. Phonons are interacting among them through *normal* and *umklapp* processes. Normal processes do not produce thermal resistance, but are mixing the phonon states. The umklapp processes are producing resistivity and, for this reason, are important at high temperatures. For these processes, we have the conservation rules of momentum $\mathbf{q} + \mathbf{q}' = \mathbf{q}'' + \mathbf{g}$ and energy $\hbar\omega + \hbar\omega' = \hbar\omega''$. Note that, in the conservation of momentum we find $\mathbf{g}$, which is a vector of the reciprocal lattice. For this reason, $\mathbf{q}$" must be large enough to fulfil the conservation of energy, with an energy equal to the sum of the energies of phonons $\mathbf{q}$ and $\mathbf{q}$', whereas the momentum is supplied by lattice. However, to have a population of high-energy phonons we must be at high temperatures.

When temperature is low, the mean free path of phonons corresponds to the size of the crystal. Let us suppose a cylindrical sample having diameter D; the mean free path is $\Lambda = D$ and then the thermal conductivity κ has the following proportionality:

$$\kappa \propto T^3 D \tag{16}$$

It is caused by the behavior of the specific heat, which is proportional to the cube of temperature. However, normal and umklapp processes become relevant at high temperature, and then we need a different proportionality to cover all the range of temperature.

This proportionality is given by:

$$\kappa \propto T^3 e^{(-\beta\Theta/k_B T)} \tag{17}$$

Therefore, (17) tells us that, in the range of low temperatures, the thermal conductivity increases with temperature, because the number of phonons is increasing with it. After reaching a maximum value, the conductivity starts decreasing because the number of scattering processes is increasing with temperature.

Besides the effect of the size of the sample and of phonon-phonon interaction, other mechanisms are scattering phonons. For instance, in a perfect lattice made of atoms of the same element, we can have atoms with different isotopic masses. Mass differences are small but they are sources of phonon scattering. Using a simple elastic theory, it is possible to find a Rayleigh scattering formula for the cross section σ of the diffusion from a point-like mass δ*M* in a medium having density ρ, for waves with wave-number *q* [1]:

$$\sigma(q) = \frac{q^4}{4\pi\rho^2}(\delta M)^2 \tag{18}$$

The cross section is linked to the mean free path as $a^3 = \sigma\Lambda$, where *a* is the lattice constant. If each atom can differ of the same quantity, we have:

$$\Lambda(q) = \frac{4\pi}{a^3 q^4}\frac{M^2}{(\delta M)^2} \tag{19}$$

$\Lambda(q)$ is strongly depending on *q*. The thermal conductivity κ can be evaluated as [1]:

$$\kappa = \frac{1}{3}\int C(q)v(q)\Lambda(q)\,d\mathbf{q} \tag{20}$$

The integration runs on all the values of the wave-number.

Integral (20) is divergent when *q* goes to zero. This happens because specific heat and velocity are constant when *q* goes to zero, then we have:

$$\kappa \propto \int \frac{q^2 dq}{q^4} \propto \int \frac{dq}{q^2} \tag{21}$$

However, phonon-phonon normal processes exist at low temperatures. These processes are not resistive, but they are mixing the phonon states. In this manner, the long-wavelength modes, which are modes scarcely diffused by isotopic defects, are transformed by the normal processes in modes having shorter wavelengths and then easily diffused.

Let us consider a specific wavenumber, given by:

$$\bar{q} \approx \frac{T}{\Theta} q_D \tag{22}$$

In (22), we find the Debye wave-number q_D and the Debye temperature Θ. We have that [11]:

$$\Lambda \approx \Lambda(\bar{q}) \propto T^{-4} \tag{23}$$

Then, the thermal conductivity κ influenced by the isotopic scattering has the following decreasing behavior with temperature:

$$\kappa \propto \left(\frac{M}{\delta M} \right)^2 \frac{1}{T} \tag{24}$$

Thermal current and relaxation times. Let us consider again the thermal current density, given by the microscopic relation [15]:

$$\mathbf{U} = \frac{1}{\Omega} \sum_{\mathbf{q}p} n_{\mathbf{q}p} \hbar \omega_{\mathbf{q}p} \mathbf{v}_{\mathbf{q}p} \tag{25}$$

Since the group velocity is given as

$$\mathbf{v}_{\mathbf{q}p} = \frac{\partial \omega_{\mathbf{q}p}}{\partial \mathbf{q}} \tag{26}$$

we have that, for acoustic phonons, (26) is simply $\mathbf{v}_{\mathbf{q}p} = c_p \hat{\mathbf{q}}$, where c_p is the speed of the sound for the given polarization of the wave and $\hat{\mathbf{q}}$ is the unit vector of $\mathbf{q}$. In the general case, to evaluate the thermal conductivity we need the dispersion of angular frequency $\omega_{\mathbf{q}p}$, in reference to the wave-number. The main difficulty in evaluating (25) is the determination of the phonon distribution $n_{\mathbf{q}p}$. Let us try to use relaxation times for this task.

The relaxation time approximation consists in writing the derivative of the distribution with respect to time as [1]:

$$\frac{\partial n_{\mathbf{q}p}}{\partial t} = \frac{n^o_{\mathbf{q}p} - n_{\mathbf{q}p}}{\tau(\mathbf{q}, p)} \tag{27}$$

$n^{o}_{\mathbf{q}p}$ is the equilibrium distribution. In (27) we see the relaxation time for the mode (**q**, *p*). If there is a thermal gradient, from the Boltzmann equation:

$$\frac{\partial n_{\mathbf{q}p}}{\partial t} = \mathbf{v}_{\mathbf{q}p} \cdot \nabla T \left(\frac{\partial n_{\mathbf{q}p}}{\partial T} \right) \tag{28}$$

In a further approximation:

$$\left(\frac{\partial n_{\mathbf{q}p}}{\partial T} \right) = \left(\frac{\partial n^{o}_{\mathbf{q}p}}{\partial T} \right) \tag{29}$$

In (29), the variation of the distribution with respect to the temperature is evaluated through the equilibrium distribution. This is possible if we are considering a small gradient of temperature.

From (27) and (28), Joseph Callaway defined the difference between the distribution existing when there is a temperature gradient and that of equilibrium as [16-18]:

$$n_{\mathbf{q}p} - n^{o}_{\mathbf{q}p} = -\tau(\mathbf{q}, p)\ \mathbf{v}_{\mathbf{q}p} \cdot \nabla T\ \frac{\hbar\omega_{\mathbf{q}p}}{k_B T^2} \frac{e^x}{(e^x - 1)^2} \tag{30}$$

In (30), we used again the dimensionless variable $x = \hbar\omega_{\mathbf{q}p} / k_B T$. The thermal current is given by:

$$\mathbf{U} = -\frac{1}{\Omega} \sum_{\mathbf{q}p} \tau(\mathbf{q}, p) \mathbf{v}_{\mathbf{q}p} \cdot \nabla T\ \frac{(\hbar\omega_{\mathbf{q}p})^2}{k_B T^2} \frac{e^x}{(e^x - 1)^2} \mathbf{v}_{\mathbf{q}p} \tag{31}$$

In the case of anisotropic solids, we have a tensor for the thermal conductivity:

$$\kappa_{\alpha\beta} = \frac{1}{\Omega} \sum_{\mathbf{q}p} \tau(\mathbf{q}, p) \frac{(\hbar\omega_{\mathbf{q}p})^2}{k_B T^2} \frac{e^x}{(e^x - 1)^2} (\mathbf{v}_{\mathbf{q}p})_\alpha (\mathbf{v}_{\mathbf{q}p})_\beta \tag{32}$$

α and β are corresponding to spatial components x,y,z. If we use the specific heat:

$$C_{ph}(\omega) = \frac{d}{dT} \left(\hbar\omega_{\mathbf{q}p} n^{o}_{\mathbf{q}p} \right) = \frac{(\hbar\omega_{\mathbf{q}p})^2}{k_B T^2} \frac{e^x}{(e^x - 1)^2} \tag{33}$$

We have:

$$\kappa = \frac{1}{\Omega}\sum_{\mathbf{q}p}\tau(\mathbf{q},p)C_{ph}(\omega)\mathbf{v}_{\mathbf{q}p}^2\cos^2\theta \tag{34}$$

In the isotropic case, θ is the angle between the group velocity and the thermal gradient. Instead of the summation on the phonon states, we use an integration [15]:

$$\frac{1}{\Omega}\sum_{\mathbf{q}p} \rightarrow \frac{1}{(2\pi)^2}\sum_p\int d\mathbf{q}$$

Ω is the volume of crystal. Then:

$$\kappa = \frac{1}{(2\pi)^2}\sum_p\int d\mathbf{q}\,\tau(\mathbf{q},p)\,C_{ph}(\omega)\,v_{\mathbf{q}p}^2\cos^2\theta \tag{35}$$

Let us assume a general relaxation time $\tau(q)$ as a function $\tau(q) = Aq^{-n}$, then the thermal conductivity that we obtain is:

$$\kappa \propto T^{3-n}\int_0^{\Theta/T}\frac{x^{4-n}e^x}{(e^x-1)^2}dx \tag{36}$$

In the next section, we will discuss in detail how Callaway used the relaxation times, to evaluate the thermal conductivity in dielectric solids.

Callaway theory. In 1959, Joseph Callaway proposed his model of thermal conductivity based on the relaxation time approximation, for investigating, in particular, the role of isotopic defects. This model is still used today to fit the experimental data of thermal conductivity; in it, also the phonon-phonon normal and umklapp processes are considered. Here, our discussion of Callaway model is based on his papers published in the Physical Review [16-18]. The formula for thermal conductivity that Callaway obtained is the following:

$$\kappa = \frac{c^2}{2\pi^2}\int\tau_c\left(1+\frac{\beta}{\tau_N}\right)C_{ph}\,q^2dq \tag{37}$$

τ_c is a combination of relaxation times coming from the different scattering processes of phonons: boundary scattering, isotope effects, normal and umklapp processes for instance. C_{ph} is specific heat. τ_N is the relaxation time approximation coming from normal processes. β is given by the following formula:

$$\beta = \frac{\int_0^{\Theta/T} \frac{\tau_c}{\tau_N} \frac{e^x}{\left(e^x - 1\right)^2} x^4 dx}{\int_0^{\Theta/T} \frac{1}{\tau_N}\left(1 - \frac{\tau_c}{\tau_N}\right) \frac{e^x}{\left(e^x - 1\right)^2} x^4 dx} \tag{38}$$

Θ is the Debye temperature and $x = \hbar\omega_{\mathbf{qp}} / k_B T$. Let us consider a relaxation time given by:

$$\tau_u^{-1} = A\omega^4 + B_1 T^3 \omega^2 + c/L \tag{39}$$

Term $A\omega^4$ represents a phonon scattering from point-like impurities and isotope defects. Term $B_1 T^3 \omega^2$ concerns the *umklapp* processes (B_1 contains the exponential factor in (17), which depend on temperature); c/L is the scattering from the boundary of the sample (c is the speed of the sound and L the size of the sample). In the case of a pure sample, A=0.

Let us assume for normal scattering:

$$\tau_N^{-1} = B_2 T^3 \omega^2 \tag{40}$$

B_2 does not depend on temperature. Combining (39) and (40), we have:

$$\tau_c^{-1} = A\omega^4 + \left(B_1 + B_2\right) T^3 \omega^2 + \frac{c}{L} \tag{41}$$

Callaway gives the thermal conductivity as:

$$\kappa = \frac{k_B}{2\pi^2 c}\left(I_1 + \beta I_2\right) \tag{42}$$

$$I_1 = \int_0^{k_B\Theta/\hbar} \tau_c \frac{\hbar^2\omega^2}{k_B^2 T^2} \frac{e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2} \omega^2 d\omega \tag{43}$$

$$I_2 = \int_0^{k_B\Theta/\hbar} \frac{\tau_c}{\tau_N} \frac{\hbar^2\omega^2}{k_B^2 T^2} \frac{e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2} \omega^2 d\omega \tag{44}$$

Let us use dimensionless variable $x = \hbar c q / k_B T$. We have:

$$I_1 = \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\Theta/T} \frac{x^4}{\left(Dx^4 + Ex^2 + \frac{c}{L}\right)} \frac{e^x}{\left(e^x - 1\right)^2} dx \tag{45}$$

In (45), we have:

$$D = A\left(\frac{k_B T}{\hbar}\right)^4 \; ; \; E = (B_1 + B_2) T^3 \left(\frac{k_B T}{\hbar}\right)^2$$

At low temperatures, it is the boundary scattering which is dominating with its relaxation time c/L; in this manner, approximating (45) with an integral from 0 to infinite, Callaway obtained:

$$I_1 = \frac{4\pi^2}{15} \frac{L}{c} \left(\frac{k_B T}{\hbar}\right)^3 \left[1 - \frac{20\pi^2}{7} \frac{EL}{c} - 16\pi^4 \frac{DL}{c}\right] \tag{46}$$

Neglecting βI_2, the thermal conductivity is approximated as (Equation 23 of Ref.18):

$$\kappa = \frac{2k_B \pi^2 L}{15c^2} \left(\frac{k_B T}{\hbar}\right)^3 \left[1 - 16A\left(\frac{\pi k_B T}{\hbar}\right)^4 \frac{L}{c} - \frac{20}{7}(B_1 + B_2) T^3 \left(\frac{\pi k_B T}{\hbar}\right)^2 \frac{L}{c}\right] \tag{47}$$

And also, in the case that *D=0*, we can have (Equation 26 of Ref.18):

$$I_1 = \left(\frac{k_B T}{\hbar}\right)^3 \frac{1}{E} \int_0^{\Theta/T} \frac{x^4}{x^2 + c/LE} \frac{e^x}{\left(e^x - 1\right)^2} dx \tag{48}$$

From this integral, Callaway deduced the following formula [18]:

$$\begin{aligned} I_1 &= \left(\frac{k_B T}{\hbar}\right)^3 \frac{1}{E} \left[\frac{1}{3}\pi^2 - e^{-\Theta/T}\left(\frac{\Theta^2}{T^2} + \frac{2\Theta}{T} + 2\right) - \frac{\pi}{2}\left(\frac{c}{LE}\right)^{\frac{1}{2}}\right] = \\ &= \frac{k_B \pi^2}{3\hbar(B_1 + B_2)T^2} \left\{1 - \frac{3e^{-\Theta/T}}{\pi^2}\left(\frac{\Theta^2}{T^2} + \frac{2\Theta}{T} + 2\right) - \frac{3\hbar}{2\pi k_B T^{\frac{5}{2}}}\left[\frac{c}{L(B_1 + B_2)}\right]^{\frac{1}{2}}\right\} \end{aligned} \tag{49}$$

As a consequence, the thermal conductivity in isotopically pure materials has a behaviour with temperature as T^{-2}, at low temperatures. The Callaway's theory was applied in [18], to the analysis

of experimental data of thermal conductivity in Germanium, in the case of normal Ge and in the case of single isotope Ge [19], showing a remarkable agreement between theory and experiments. In fact, Callaway's paper was among the first works to point out the importance of the isotope scattering in reducing the thermal conductivity.

After this discussion on the theory concerning the Boltzmann equation for phonons and its solution in the relaxation time approximation, in a next paper, we will address how the thermal conductivity evaluated in this framework is in agreement with experimental data.

References

[1] Ziman, J.M. (1962). Electrons and phonons: The theory of transport phenomena in solids. Clarendon Press. Reprint Edition in 2001. ISBN-10: 0198507798, ISBN-13: 978-0198507796

[2] Gurevich, V.L. (1986). Transport in phonon systems. North-Holland. ISBN-10: 044487013X, ISBN-13: 978-0444870131

[3] Srivastava, G.P. (1990). The physics of phonons. Taylor and Francis. ISBN ISBN-10: 0852741537, ISBN-13: 978-0852741535

[4] Omini, M., & Sparavigna, A. (1995). An iterative approach to the phonon Boltzmann equation in the theory of thermal conductivity. Physica B, 212(2), 101-112. DOI: 10.1016/0921-4526(95)00016-3

[5] Omini, M., & Sparavigna, A. (1997). Effect of phonon scattering by isotope impurities on the thermal conductivity of dielectric solids. Physica B, 233(2-3), 230-240. DOI: 10.1016/s0921-4526(97)00296-2

[6] Omini, M., & Sparavigna, A. (1996). Beyond the isotropic-model approximation in the theory of thermal conductivity. Physical Review B, 53(14), 9064-9073. DOI: 10.1103/physrevb.53.9064

[7] Omini, M., & Sparavigna, A. (1997). Heat transport in dielectric solids with diamond structure. Nuovo Cimento D, 19(10), 1537-1564.

[8] Sparavigna, A. (1997). Thermal conductivity of solid neon: an iterative analysis. Physical Review B, 56(13), 7775-7778. DOI: 10.1103/physrevb.56.7775

[9] Sparavigna, A.C. (2015). Thermal conductivity of zincblende crystals. Mechanics, Materials Science & Engineering Journal, October 2015, 1-8. DOI: 10.13140/RG.2.1.1758.0565

[10] Broido, D.A., Ward, A., & Mingo, N. (2005). Lattice thermal conductivity of silicon from empirical interatomic potentials. Physical Review B, 72(1), 014308. DOI: 10.1103/physrevb.72.014308

[11] Kaburaki, H., Li, J., Yip, S., & Kimizuka, H. (2007). Dynamical thermal conductivity of argon crystal. Journal of Applied Physics, 102(4), 043514. DOI: 10.1063/1.2772547

[12] Turney, J.E., Landry, E.S., McGaughey, A.J.H., & Amon, C.H. (2009). Predicting phonon properties and thermal conductivity from anharmonic lattice dynamics calculations and molecular dynamics simulations. Physical Review B, 79(6), 064301. DOI: 10.1103/physrevb.79.064301

[13] McGaughey, A.J., & Kaviany, M. (2004). Quantitative validation of the Boltzmann transport equation phonon thermal conductivity model under the single-mode relaxation time approximation. Physical Review B, 69(9), 094303. DOI: 10.1103/physrevb.69.094303

[14] Li, W., Carrete, J., Katcho, N.A., & Mingo, N. (2014). ShengBTE: A solver of the Boltzmann transport equation for phonons. Computer Physics Communications, 185(6), 1747-1758. DOI: 10.1016/j.cpc.2014.02.015

[15] Ashcroft, N.W., & Mermin, N.D. (1976). Solid state physics. Saunders College Publishing. ISBN-10: 0030839939, ISBN-13: 978-0030839931

[16] Callaway, J. (1961). Low-temperature lattice thermal conductivity. Physical Review, 122(3), 787-790. DOI: 10.1103/physrev.122.787

[17] Callaway, J., & von Baeyer, H.C. (1960). Effect of point imperfections on lattice thermal conductivity. Physical Review, 120(4), 1149-1154. DOI: 10.1103/physrev.120.1149

[18] Callaway, J. (1959). Model for lattice thermal conductivity at low temperatures. Physical Review, 113(4), 1046-1051. DOI: 10.1103/physrev.113.1046

[19] Geballe, T.H., & Hull, G.W. (1958). Isotopic and other types of thermal resistance in Germanium. Physical Review, 110, 773-775. DOI: 10.1103/physrev.110.773